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Energy transfer from Gd^{3+} to Cr^{3+} in $Cr^{3+}:Gd_3Sc_2Ga_3O_{12}$ (GSGG)

S.K. Vargas, D.S. Hamilton*

Department of Physics, 2152 Hillside Road, University of Connecticut, Storrs, CT 06269-3046, USA

Abstract

The temporal characteristics and temperature dependence of the Gd^{3+} to Cr^{3+} energy transfer in Cr^{3+}:GSGG are presented. Following pulsed excitation of the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition in Gd^{3+}, the risetime of the resulting Cr^{3+} fluorescence was used to determine the Gd^{3+} to Cr^{3+} energy transfer rate. The results indicate a rapid energy migration among the Gd^{3-} ions followed by a Gd^{3+} to Cr^{3+} energy transfer step over a single fixed distance.

Keywords: Energy transfer; Gd^{3-}; Cr^{3+}; GSGG

Excitation spectra of Cr^{3+}:GSGG in the near ultraviolet obtained by monitoring the Cr fluorescence indicate efficient Gd to Cr energy transfer [1, 2]. In the results presented here, we have measured the dynamics of this energy transfer process by pumping the $^6P_{7/2}$ level of Gd with a frequency-doubled pulsed dye laser at 313 nm. The resulting broad-band Cr^{3+} fluorescence was detected using a photomultiplier tube and a SR430 multichannel scalar/averager for photon counting, resulting in time-dependent measurements with a dynamic range of 3–4 order of magnitude. The laser pulse width was 10 ns and the SR430 was used with 40 ns or 320 ns time bins. The Cr:GSGG sample was grown by Union Carbide and had a nominal 1 at% Cr concentration.

The time dependence of the Cr fluorescence is characterized by a rapid rise followed by a much slower decay. The decay of the fluorescence is exponential over at least three orders of magnitude. There was however a small background signal following the laser pulse that was larger than the prepulse value, indicating perhaps a small additional lifetime component due to the cation-exchange structural disorder. The measured decay times and their temperature dependence agree well with those of Healy et al. [3] for direct pumping of the Cr^{3+} ions.

Fig. 1 illustrates the initial rise of the Cr^{3+} fluorescence immediately following the pulsed laser excitation of the $^6P_{7/2}$ level of Gd^{3+}. This initial rise of the Cr^{3+} fluorescence is exponential in character and the data was fit to

$$N(t) = N_{\max} e^{-t/T_d}(1 - e^{-t/T_r}) + N_b, \tag{1}$$

where T_d is the Cr decay time, T_r is the rise time and N_b is a constant background count. Assuming $\sqrt{N}$ counting statistics, near-unity values for χ^2 using this fitting function were obtained. The model is consistent with the one where the Gd to Cr transfer is described by a single transfer rate indicating a transfer over a single fixed distance. This

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* Corresponding author. Fax: +(860) 486-3346; e-mail: hamilton@phys.uconn.edu.

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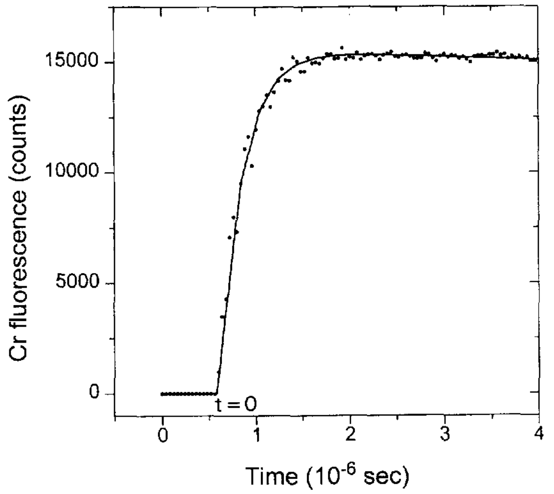

Fig. 1. The short-time dynamics of the Cr emission following 312 nm excitation of Gd^{3+} at 300 K. The solid line represents the fit to the data giving a rise time of 310 ± 10 ns. The laser pulse is at 580 ns.

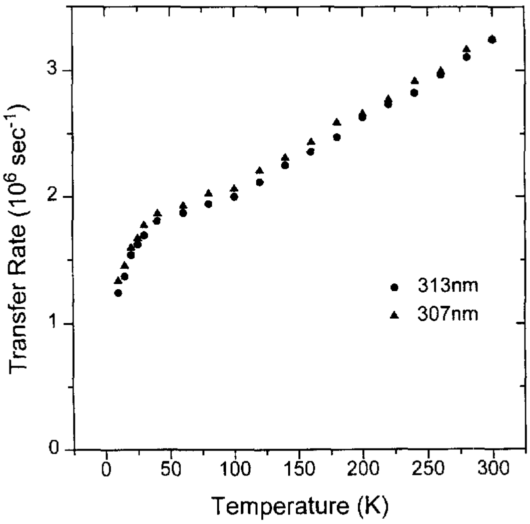

Fig. 2. Transfer rate from Gd to Cr as a function of temperature. A linear relationship is obtained for the temperatures above 100 K.

then indicates that there is a rapid migration of the excitation on the gadolinium sublattice which precedes the Gd to Cr transfer. Exchange interaction has been found to increase the Gd to Gd transfer considerably, which enhances the energy migration. For Gd–Gd distances less than 4 Å, the exchange interactions seems to govern the energy transfer process [4, 5]. In GSGG, this distance is 3.85 Å, suggesting that the exchange interactions dominate the energy migration process.

The temperature dependence of the Gd to Cr transfer rate defined as $W = 1/T_r$, assuming that the Gd radiative decay rate in the absence of the Cr ions is much less than W, was measured from 10 K to 300 K and the results are shown in Fig. 2. The temperature dependence shows two distinct regions. At temperatures above 100 K, the transfer rate increases linearly with temperature. But in the region below 100 K, a much stronger temperature dependence is observed. The data suggest that the overall temperature dependence is a product of two terms. The first being the migration among the Gd ions that increases quickly with increasing temperature and then saturates and the second being the linear Gd to Cr rate, suggesting a one-phonon mediated process.

Nearly identical results for the Gd to Cr energy transfer were obtained following excitation of the higher lying Gd $^6P_{5/2}$ level at 307 nm. However, pumping of the ^6I manifold at 277 or 274 nm produced transfer times of 65 ± 10 ns which were approximately temperature independent between 10 and 300 K. The ^6I manifold is quasi-resonant with a charge transfer band in Cr^{3+} and the transfer times may suggest a more resonant interaction between the Gd^{3+} and Cr^{3+} ions.

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